Electrochemistry of Nanoporous Graphene for Lithium-Oxygen Batteries

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論 文 内 容 要 旨

Non-aqueous rechargeable lithium-oxygen ($Li\text{-}O_2$) batteries are emerging as a new paradigm for high-density electrical energy storage because of the ultrahigh theoretical energy density (3,500 Wh/kg). Basing on the reversible redox reaction of $2Li + O_2 \leftrightarrow Li_2O_2$, $Li\text{-}O_2$ batteries release electrochemical energy by reducing gaseous oxygen from the atmosphere to form insulating solid Li_2O_2 in discharging and are recovered by oxidizing/decomposing Li_2O_2 in charging. Since multi-phases (gas, liquid, solid) are involved into the $Li\text{-}O_2$ battery reactions, the cathodes are expected to have open porosity, high conductivity and high catalytic activity, together with good electrochemical stability, light weight and mechanical flexibility. Developing high performance porous cathodes that facilitate highly efficient O_2/Li_2O_2 redox reactions in the aprotic media is very critical for the practical implementation of non-aqueous $Li\text{-}O_2$ batteries. In this backdrop, the present thesis work aims to develop advanced three-dimensional (3D) nanoporous graphene materials, and on basis of understanding the fundamental electrochemistry of the cathodic reactions, to develop high-performance nanoporous graphene based $Li\text{-}O_2$ batteries.

A nanoporous metal based chemical vapor deposition (CVD) method was employed for synthesizing the novel 3D bicontinuous nanoporous graphene materials. Briefly, nanoporous Ni prepared by dealloying a $Ni_{30}Mn_{70}$ sheet was used as both catalyst and porous template for the CVD growth of graphene at 800-1000°C using benzene, pyridine or thiophene as the precursor. Free-standing nanoporous graphene sheets were obtained after dissolving the nanoporous Ni substrates with hydrochloric acid and then dried by supercritical CO_2. The samples were systematically characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), surface area tests, and physical property measurements. The nanoporous graphene possesses unique properties of interconnected open porosity (> 95%), large accessible surface area (ca. 700-1200 $m^2 g^{-1}$) and high conductivity (ca. 1.2×10^4

S m^{-1}). By using different organic precursors for graphene growth, heteroatoms of nitrogen and sulfur have been successfully doped into the nanoporous graphene to functionalize its catalytic properties. The nanoporous metal based CVD method also provided flexibility in tailoring the pore sizes (200-1000 nm) and dimensions (with thickness ranging from 5 to 100 μm) of the nanoporous graphene by changing the graphene growth or pre-annealing temperatures and using $Ni_{30}Mn_{70}$ sheet with different dimensions.

A non-aqueous three-electrode electrochemical system, which consists of a disk working electrode, a lithium metal counter electrode and a non-aqueous silver quasi-reference electrode, was developed and utilized for investigating the fundamental Li-O_2 electrochemistry in Li-O_2 battery cathodes. Cyclic voltammetry study showed that the reduction of O_2 to Li_2O_2 proceeds by multi-step reactions via the formation of a LiO_2 intermediate; while in the oxygen evolution reaction (OER), Li_2O_2 is directly oxidized to oxygen without going through LiO_2. Rotating disk electrode measurements further confirmed the formation of a LiO_2 intermediate in the oxygen reduction reaction (ORR). It was also demonstrated that the LiO_2 formation process determines the kinetics of ORR and has a Tafel slope of 120 mV dec^{-1}. The effect of chemical doping on the reaction kinetics of nanoporous graphene for Li-O_2 battery was also investigated by cyclic voltammetry, rotating disk electrode measurements and electrochemical impedance spectroscopy. It was shown that chemical doping by N and S can enhance the catalytic activity of nanoporous graphene for Li-O_2 reactions: N-doping obviously enhances the ORR kinetics and S-doping promotes the OER activity.

The bicontinuous nanoporous graphene was successfully used as cathodes for rechargeable Li-O_2 batteries. Experimentally the centimeter-sized free-standing and flexible nanoporous graphene sheet was directly installed into a Li-O_2 battery without the requirements of complex assembly and binder. With a 1.0 M LiTFSI in tetraethylene glycol dimethyl ether (TEGDME) electrolyte, the Li-O_2 batteries delivered large and recoverable capacities up to ca. 10,400 mAh g^{-1}. A combination of X-ray diffraction (XRD), SEM and TEM characterizations confirmed that the large recoverable capacity is based on highly reversible Li_2O_2 formation and decomposition reactions. The unique bicontinuous porous structure of nanoporous graphene also benefits efficient diffusion of oxygen and ions, giving rise to full utilization of the porosity and very uniform distribution of Li_2O_2 particles in the electrode after discharge. The efficient mass transport also results in a weak dependence of the battery performance on the cathode thickness. It has been shown that chemical doping of nanoporous graphene has an obvious effect on the battery property. N-doping gives rise to a very large discharge capacity and S-doping favors a stable cycling behavior. The nanoporous S-doped graphene based Li-O_2 battery delivers an excellent cycling stability of long lifetimes up to 300

discharge-charge cycles at the cut-off capacity of 1000 mAh g^{-1} and 100 cycles at 2000 mAh g^{-1}, which correspond to the total working time of 2000 and 1333 hours, respectively. The outstanding property of the S-doped graphene benefits from high stability of the sulfur dopants, enhanced reaction kinetics of Li_2O_2 oxidation, and the slow accumulation of side products.

In an effort to develop a full-performance Li-O_2 battery, the nanoporous graphene electrode was further integrated with a compatible redox mediator. Cyclic voltammetry studies demonstrated the effective role of tetrathiafulvalene in facilitating the decomposition of Li_2O_2 at a significantly decreased charge potential. Stable cycling up to 100 discharge-charge cycles at large capacities (up to 2000 mAh g^{-1}), high rates (up to 2000 mA g^{-1}) and a low charge potential (~3.5 V) have been simultaneously realized in a single Li-O_2 battery. The tetrathiafulvalene-induced low charge potential has also given rise to much less side reactions in comparison with those in the absence of redox mediator, as evidenced by the significantly reduced amounts of alkylcarbonate and Li_2CO_3 in the nanoporous graphene cathode after long cycling tests. To demonstrate the capability of practical implementation of the nanoporous graphene based Li-O_2 batteries, a Li-O_2 pouch battery prototype with a size of about 28 mm × 40 mm × 1.4 mm was developed. Two pieces of large sized nanoporous graphene sheets were assembles face-to-face as the cathodes, with a Li metal foil sandwiching between them as the anodes. The Li-O_2 pouch cells well resemble the excellent properties that have been achieved with coin cells, deliver robust discharge/charge cycling at 1000 mAh g^{-1} and 1000 mA g^{-1} for 100 cycles with quasi-constant discharge/charge potentials and high energy efficiency. Remarkably, the Li-O_2 pouch battery prototype affords a large maximum discharge capacity of 26,840 mAh g^{-1} at a rate of 200 mA g^{-1}, which, when normalized by the total mass of the pouch cell, corresponds to a gravimetric capacity of 95.70 mAh g^{-1}_{cell} and an energy density of 260.30 Wh kg^{-1}_{cell}, surpassing those of commercial Li-ion polymer batteries.

論文審査結果の要旨

Li-O_2電池は、従来のリチウム2次電池に比べて、高いエネルギー密度を兼ね備えていることから研究が盛んに行われている。しかしながら、空気中で安定に動作するための多孔質カソード電極の開発が必要であり容易ではない。韓 久慧氏は、ナノポーラス金属基板を活用することで高品質なナノポーラスグラフェンを系統的に作製し、ドーパント（N, S）を導入して触媒活性度を向上させることで、高エネルギー密度とサイクル寿命特性を兼ね備えたLi-O_2電池の開発に繋げた。

論文は6つの章で構成されており、概要は以下のとおりであった。

第1章　リチウム空気電池の動作原理

従来のリチウム2次電池と比較し、カソード電極における過酸化リチウム(L_2O_2)の生成によって動作する仕組みを説明した。

第2章　ナノポーラスグラフェンの作製方法

ナノポーラスニッケルを基板として用いて、化学蒸着法(CVD)で表面にベンゼンを前駆体としてグラフェンを成長させる。その後、酸でニッケルを除去した後に、CO_2の超臨界現象を利用して乾かして作製した。また、ドーパント（N, S）の導入をベンゼンのかわりにピリジンやチオフェンを利用することで導入した。すべての試料のラマンスペクトルでグラフェンの特長である2Dバンドピークが確認された。

第3章　ナノポーラスグラフェンを用いたLi-O_2の電気化学研究

基礎的な電気化学反応を理解するために、非水溶系の3極セルを設計した。これによって、過酸化リチウムの形成過程とその電位について知ることができた。また、Tafelプロットによる律速過程の同定、ドーパントの影響、ナイキスト分析による抵抗成分の抽出などを行った。

第4章　ナノポーラスグラフェンを用いたLi-O_2電池の評価

実際にLi-O_2空気電池セルのカソード電極にナノポーラスグラフェンを組み込んで評価を行った。ドーパント導入による過電圧の低下とサイクル寿命特性の向上を行った。特に、Sドープしたもののサイクル寿命特性が高かった。これはL_2O_2の酸化促進による効果だと考えられる。容量では最大で~10,400 mAh g^{-1}に到達し、1000 mAg^{-1}の容量を300回充放電することに成功した。

第5章　酸化還元緩衝材の添加によるナノポーラスグラフェンを用いたLi-O_2電池の評価

酸化還元緩衝材としてしられるTFT(tetrathiafulvalene)は、過電圧の低下することが期待されたがメカニズムについては不明であった。そこで、第3章の3極セルによってその基礎電気化学反応を明らかにした。そして実際にポーチ型の薄いLi-O_2空気電池に作り、現在のリチウムイオン電池よりも重量あたりの電気容量とエネルギー密度が勝っていることを実証した。

第6章　結言

簡潔に結果がまとめられた。

このように、本論文はナノポーラスグラフェンを基軸にした高いエネルギー密度とサイクル寿命特性を兼ね備えたLi-O_2電池の開発に成功した先駆的研究であり、論文構成も妥当である。このような詳細な検討は、韓 久慧氏の電気化学における高い専門知識と独自性により構築・展開されたものであり、研究者としての極めて高い資質を示している。

よって、本論文は博士(工学)の学位論文として合格と認める。